

POSSIBLE MECHANISM FOR SULFUR MASS INDEPENDENT FRACTIONATION IN THE B-X UV TRANSITION OF S₂

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Anomalous sulfur isotope ratios, called mass independent fractionation (MIF), are commonly observed in sedimentary rocks formed more than 2.5 billion years ago. These anomalies likely originated from photochemistry of small, sulfur-containing molecules in the early Earth's atmosphere. The disappearance of MIF in rocks younger than 2.5 billion years is thought to be evidence of rising O₂ concentrations during the Great Oxygenation Event (GOE), an important milestone in the development of life on Earth. However, the photochemical origin of the pre-GOE anomaly is not well understood. Here, we use a model of the X, B, and B'' states of S₂, originally developed by Western, to determine a possible mechanism for isotopologue-selective photodissociation. A model of the rotation-vibration structure of the B-X UV transition shows small perturbations between the bright B state and the dark B'' state that vary depending on isotopologue. These perturbations suggest a sequential two-photon mechanism for selective photodissociation. Symmetry (e.g., 32-32 vs. 32-34) may also contribute to MIF. This presentation will primarily focus on the UV spectra of the 32-32 and 32-34 isotopologues. We also examine the possibility that a similar mechanism may be at work in the B-X transition of SO.